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Electrical conductivity fluctuations in superionic solids provide a new way of examining transport and electrode properties of solid electrolytes. Of particular interest are the Naβ and Naβ"aluminas because of their high ionic conductivity, potentially important technological applications, and the ease with which the mobile sodium ions can be exchanged for a number of mono- and di-valent cations. Single crystal and ceramic specimens of sodium, silver, lead, and calcium β"aluminas, as well as mixed Na/Ag and Na/Ca conductors, have been found to exhibit conductivity fluctuations associated with diffusion of the mobile ions. Also, in the absence of electric current and at frequencies above about 100 Hz Nyquist noise corresponding to the bulk electrolyte resistance is observed. Below 100 Hz noise associated with amalgamation reactions at the electrolyte/contact interface or noise associated with ionic shot noise during the build-up of an electric double layer at the interface are dominant. Experimental diffusion noise levels can be quantitatively explained by focusing on the diffusion of ion-vacancy pairs in single conduction planes. Fluctuations in adjacent planes are correlated and correlations arising from in-plane coulomb forces are negligible.

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Final Report

CONDUCTIVITY FLUCTUATIONS IN FAST IONIC CONDUCTORS

by

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1 August 1982 through 30 September 1990

CONDUCTIVITY FLUCTUATIONS IN FAST IONIC CONDUCTORS

FINAL REPORT

This project has studied electrical conductivity fluctuations in superionic solids as a way of understanding transport and electrode properties of solid electrolytes. The research effort has concentrated on the Naβ and Naβ"aluminas because of their high ionic conductivity, potentially important technological applications, and the ease with which the mobile sodium ions can be exchanged for a number of mono- and di-valent cations. Both single crystal and ceramic specimens of sodium, silver, lead, and calcium β"alumina have been examined, as well as mixed Na/Ag and Na/Ca conductors.

The research results obtained on the project have been reported in the 21 Technical Reports and 19 published papers listed in the following pages. Briefly, three different electrical noise processes are observed in both single crystal and ceramic samples. In the absence of electric current and at frequencies above about 100 Hz Nyquist noise corresponding to the bulk electrolyte resistance is observed. This makes it possible to measure electrolyte conductivity in equilibrium and over a range of frequencies free from interfering contact effects. Below 100 Hz noise associated with amalgamation reactions at the electrolyte/contact interface is measured when amalgam contacts are employed. With other contact solutions (e.g., NaI in propylene carbonate) noise characterized as ionic shot noise during the build-up of an electric double layer at the interface is dominant.

In the presence of current, all of the solid electrolytes examined exhibit conductivity fluctuations attributable to diffusion noise of the mobile ions, which is a direct experimental proof that electrical conduction is by diffusion. The observed noise levels are much larger than predicted on the basis of a simple interpretation of the standard theory of diffusion noise, which is based on independent diffusing entities. However, it appears that by focusing on the diffusion of ion-vacancy pairs in single conduction planes, it is possible to account quantitatively for the observed noise. Furthermore, the analysis indicates that fluctuations in adjacent planes are correlated and that correlations arising from in-plane coulomb forces are negligible. A full description of this more sophisticated analysis is being prepared for publication.

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TECHNICAL REPORTS

# 1	May, 1983	Contact Noise in Superionic Ceramics
# 2	August, 1983	Elecrode Noise in Beta Aluminas
# 3	November, 1983	Internal Noise of Low-Frequency Pre-Amplifiers
# 4	May, 1984	Spectral Averaging and Low-Frequency Sampling Modifications for the IQS 401 FFT Spectrum Analyzer
# 5	November, 1984	Current Noise in Sodium Beta" Alumina Ceramic
# 6	September, 1985	Noise in Silver Beta" Alumina Ceramics
# 7	September, 1985	Noise in Sodium Beta" Alumina Crystals
# 8	August, 1986	Silver Beta" Alumina Ceramics & Single Crystals
# 9	January, 1987	Noise in Single Crystal Pb Beta" Alumina
#10	February, 1987	Contact Noise in Sodium Beta" Alumina
#11	May, 1987	Noise in Lead Beta" Alumina
#12	May, 1987	Contact Noise in Sodium Beta" Alumina
#13	June, 1987	Voltage Fluctuations at Sodium Beta" Alumina/ Mercury Electrodes
#14	November, 1987	Contact and Current Noise in Beta Alumina and Nasicon Ceramics
#15	January, 1988	The Kinetics of Contact Noise in Na Beta" Alumina
#16	June, 1988	Diffusion Noise in Na, Ag and Pb Beta" Aluminas
#17	June, 1988	Diffusion Noise in Annealed Na, Ag and Pb Beta" Aluminas
#18	July, 1988	A Review of Noise Studies in Superionic Electrolytes
#19	August, 1988	Digital Lock-in Detector for Ultra-Low Level Noise Spectrum Analysis
#20	February, 1989	Conductivity Fluctuations in Mixed Na/Ca Beta" Alumina
#21	March, 1989	Current and Thermal Noise in Mixed Na/Ag Beta"Alumina.

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